

Statistical Estimation of Diffusion Coefficients under Finite Bath, Surface Barrier Conditions

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SYNOPSIS

When surface-barrier effects are not taken into account, computation of diffusion coefficients from data obtained under finite bath conditions can lead to error. A technique is given by which the most probable diffusion coefficient and the most probable dimensionless surface barrier parameter simultaneously can be estimated for diffusant uptake by solid polymeric cylinders. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Under certain limiting assumptions, uptake of diffusants from finite baths by cylindrical polymeric solids can be described by use of the various diffusion equation solutions of Wilson,¹ Crank,² Carman-Haul,³ and Urbanik.⁴

Wilson's Equation

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1 + \alpha) \exp[-q_n^2(Dt/r^2)]}{4 + 4\alpha + \alpha^2 q_n^2} \quad (1)$$

In eq. (1), M_t/M_∞ is the fractional equilibrium uptake of diffusant by the cylinder, i.e., diffusant uptake at a given time, M_t , and at equilibrium, M_∞ . The dimensionless parameter, Dt/r^2 , consists of the diffusion coefficient, D (cm^2/s), the uptake time, t (s), and the radius of the cylinder, r (cm). The alpha term is a measure of equilibrium bath exhaustion:

$$\alpha = \frac{1 - E_\infty}{E_\infty} \quad (2)$$

where equilibrium exhaustion, E_∞ , is

$$E_\infty = \frac{C_0 - C_\infty}{C_0} \quad (3)$$

where C_0 and C_∞ are, respectively, the initial and equilibrium concentration of diffusant in the external medium. In eq. (1), the q_n 's are the positive, nonzero roots of

$$\alpha q_n J_0(q_n) + 2J_1(q_n) = 0 \quad (4)$$

in which J_0 and J_1 are zero- and first-order Bessel functions.

When bath exhaustion is very high, convergence of Wilson's equation requires an exceedingly high number of summation terms for small values of Dt/r^2 and can result in a significant decrease in accuracy. For this reason, the error function equations of Crank, Carman-Haul, and Urbanik are much more reliable when bath exhaustion is high and Dt/r^2 is low.

Crank's Equation

$$\frac{M_t}{M_\infty} = \frac{4(1 + \alpha)[1 - \exp(X^2) \text{erfc}(X)]}{4 + \alpha} \quad (5)$$

where "erfc" is the error function complement and X is

$$X = 2 \left(1 + \frac{\alpha}{4} \right) \frac{\sqrt{Dt/r^2}}{\alpha} \quad (6)$$

The equation of Carman and Haul is a slight improvement over that of Crank for small values of Dt/r^2 .

Carman and Haul's Equation

$$\frac{M_t}{M_\infty} = \frac{\gamma_3}{\gamma_3 + \gamma_4} \exp(X^2) \operatorname{erfc}(X) + \frac{\gamma_4}{\gamma_3 + \gamma_4} \exp(Y^2) \operatorname{erfc}(Y) \quad (7)$$

where

$$\gamma_3 = \frac{\sqrt{1 + \alpha} + 1}{2} \quad (8)$$

and

$$\gamma_4 = \gamma_3 - 1 \quad (9)$$

The "X" and "Y" terms of the equation of Carman and Haul are

$$X = \frac{2\gamma_3}{\alpha} \sqrt{\frac{Dt}{r^2}} \quad (10)$$

$$Y = -\frac{2\gamma_4}{\alpha} \sqrt{\frac{Dt}{r^2}} \quad (11)$$

Urbanik's equation, although somewhat more complex, is an improvement over the equations of Crank and Carman-Haul.

$$\begin{aligned} \frac{M_t}{M_\infty} = 1 &+ \frac{2(1 + \alpha) \exp(-BT)}{\alpha(X - Y)} \left[\frac{\exp(Y^2 T) \operatorname{erfc} \sqrt{Y^2 T}}{1 - B/Y^2} \right. \\ &- \frac{\exp(X^2 T) \operatorname{erfc} \sqrt{X^2 T}}{1 - B/X^2} \\ &+ \sqrt{B} \left(\frac{X}{X^2 - B} - \frac{Y}{Y^2 - B} \right) \\ &\left. \times \exp(B^2 T) \operatorname{erfc} \sqrt{B^2 T} \right] \quad (12) \end{aligned}$$

where the constant "B" is an empirical parameter, having a value of 8.42. In addition, the parameters "X" and "Y" are

$$X = \frac{4 + \alpha - \sqrt{(4 + \alpha)^2 + 16\alpha^2(B - 1.5\sqrt{B})}}{4\alpha} \quad (13)$$

$$Y = \frac{4 + \alpha + \sqrt{(4 + \alpha)^2 + 16\alpha^2(B - 1.5\sqrt{B})}}{4\alpha} \quad (14)$$

Urbanik's equation is quite valuable since it can be used for essentially all values of bath exhaustion and dimensionless time—a limitation of the equations of Crank and Carman-Haul.

Nevertheless, no matter which of the diffusion equation solutions given above that one uses, it is essential that certain assumptions about the system that one is investigating be fulfilled. Assumptions that are necessary for proper use of the analytical solutions to the diffusion equation given above are the following:

1. The diffusion coefficient is a constant, concentration-independent quantity.
2. The equilibrium distribution coefficient of the diffusant between the solid sorbent and the external bath is linear for a wide range of concentrations.
3. The solid sorbent is a morphologically stable, homogeneous endless cylinder.
4. No surface barrier exists at the cylindrical surface that would impede mass transfer of the diffusant from the external medium to the sorbent surface, i.e., no diffusional boundary layer exists.

When all four assumptions given above are satisfied, eq. (1), (5), (7), or (12) can be solved iteratively for the diffusion coefficient, D , from a knowledge of α , M_t/M_∞ at a corresponding time, t , and the radius of the polymeric solid cylinder, r . It is unfortunate that the four assumptions listed above rarely hold for real sorption systems. Quite often it is found that, even when the first three assumptions given above are found to hold, the flow of an external bath past the surface of the polymeric cylinders may be so very inefficient that a diffusional boundary layer develops at the cylindrical surface.

In the case of *infinite* bath systems, i.e., systems in which the concentration of diffusant in the external medium does not change during sorption of the diffusant by the polymeric cylinder, the boundary layer influence can be taken into account by the use of the equation of Newman.⁵

Newman's Equation

The equation of Newman can be written more concisely as

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4 \exp[-\beta_n^2(Dt/r^2)]}{\beta_n^2(1 + \beta_n^2/L^2)} \quad (15)$$

where the β_n 's are the roots of the transcendental equation:

$$\beta_n J_1(\beta_n) - L J_0(\beta_n) = 0 \quad (16)$$

in which J_0 and J_1 again are zero- and first-order Bessel functions, and the dimensionless parameter, L , is defined by⁶

$$L = \frac{D_m r}{DK\delta_D} \quad (17)$$

where D_m and D are the diffusion coefficients of the diffusant in the external medium and polymer, respectively; K , the equilibrium distribution coefficient of the diffusant between the external medium and the polymer; r , the radius of the cylinder; and δ_D , the thickness of the diffusional boundary layer—a quantity that is inversely proportional to the rate of flow of the external medium past the surface of the polymeric cylinder. When the rate of flow of the external medium is very high, the thickness of the diffusional boundary layer approaches zero and the value of “ L ” approaches infinity. When the value of “ L ” is infinity, the term β_n^2/L^2 drops out and eq. (15) becomes equivalent to Hill's equation.⁷

Hill's Equation

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{\beta_n^2} \exp[-\beta_n^2(Dt/r^2)] \quad (18)$$

In eq. (19), the positive transcendental Bessel roots are expressed by the simpler equation:

$$J_0\beta_n = 0 \quad (19)$$

NEW COMPUTATIONAL TECHNIQUE

In view of the fact that no analytical solution to the diffusion equation exists in equation form that expresses M_t/M_∞ as a function of Dt/r^2 , α , and L , a computational technique recently has been proposed to fill this mathematical void.⁸⁻¹⁰ The details of the computational procedure are given elsewhere, but may be summarized briefly as follows: Linear transitional systems are characterized by linear sorption isotherms and constant, concentration-independent diffusion coefficients. These systems are *transitional* if they are capable of changing from infinite bath to finite bath systems during the course of diffusant uptake. Such systems are distinguished from other sorption systems by having two forms of fractional diffusant uptake at the point of transition.¹¹ The two forms are fractional *equilibrium* uptake for finite

bath conditions, $(M_t/M_\infty) = f_\infty$, and fractional *saturation* uptake for infinite bath conditions, $(M_t/M_\infty) = f_{\text{sat}}$. The two quantities are related to each other for a given value of α by

$$f_{\text{sat}} = \frac{\alpha f_\infty}{1 + \alpha - f_\infty} \quad (20)$$

Under the assumption that all fractional uptake values for a finite bath system can be treated as if they were transitional values, dimensionless values of time, $(Dt/r^2)_0$, can be estimated for each value of M_t/M_∞ for given values of α and L by

$$(Dt/r^2)_0 = (Dt/r^2)_1 + [(Dt/r^2)_2 - (Dt/r^2)_3] \quad (21)$$

where $(Dt/r^2)_1$ is the value of dimensionless time calculated by the use of eq. (1), (5), (7), or (12) for a given value of f_∞ and α when L equals infinity; $(Dt/r^2)_2$ is the value of dimensionless time calculated by the use of eq. (15) for corresponding values of f_{sat} and a given value of “ L ,” when alpha equals infinity, and $(Dt/r^2)_3$ is dimensionless time calculated by the use of eq. (18) for corresponding values of f_{sat} when both α and L are equal to infinity. Hou et al.¹² used eq. (21) to prepare a series of tables of Dt/r^2 for various equally spaced values of M_t/M_∞ for several values of fractional equilibrium exhaustion, E_∞ , and dimensionless boundary layer, L . These tabular values are useful not only for interpolation but also for the development of analytical approximations that will permit the direct computation of M_t/M_∞ from a knowledge of Dt/r^2 , α , and L .

STATISTICAL ANALYSIS

Equation (21) is useful for the estimation of diffusion coefficients based on data obtained under finite bath, boundary layer conditions. However, although experimental parameters such as equilibrium bath exhaustion, E_∞ , and fractional uptake, M_t/M_∞ , at a given time, t , can be *measured*, the dimensionless boundary layer parameter, L , cannot be measured directly. In the absence of knowledge of the value of L , no estimate of the diffusion coefficient can be computed. Nevertheless, a statistical technique can be used in combination with eq. (21) to make a simultaneous estimate of the *most probable* diffusion coefficient and the *most probable* boundary layer parameter, L . The statistical method, which has been applied previously to infinite bath systems,¹³ is il-

illustrated for a finite bath, boundary layer system by the example to follow.

Real Systems

Sorption of pure Disperse Red 11 by stabilized poly(ethylene terephthalate) fiber under very efficiently stirred *infinite* bath conditions has been shown to be characterized by a constant diffusion coefficient and a linear sorption isotherm.¹⁴ Based on parameter estimates given elsewhere,¹¹ sorption of this dye at 125°C at a concentration of 0.25% based on the weight of the fiber will occur under *finite* bath conditions when the liquor-to-fiber ratio is 10/1. Under these conditions, the disperse dye is completely dissolved in the aqueous medium and the fractional equilibrium bath exhaustion, E_∞ , is equal to 0.84. Fractional dye uptake, M_t/M_∞ , as a function of time in minutes can be monitored continuously by the use of suitable spectrophotometric measurements made on the aqueous solution of the disperse dye. In view of the usual experimental variation that occurs in such measurements, the Monte Carlo estimates of M_t/M_∞ given in Table I as a function of time are not unreasonable. The data given in Table I are for a poorly stirred dyeing system in which the value of L is unknown.

Application of eq. (1), (5), (7), or (12) to the row data of the first two columns of Table I results in the corresponding diffusion coefficients of column three. It is seen that the computed diffusion coefficients of column three *increase* with increasing val-

ues of time, or M_t/M_∞ , and result in a very high coefficient of variation—even though it is known that the diffusion coefficient is *constant* for the dye/fiber system investigated. It is clear that the use of the conventional finite bath diffusion equation solutions, which assume a value of infinity for L or a value of zero for $1/L$, can lead to error when L is not equal to infinity.

When eq. (21) is applied to the data of Table I for increasing values of $1/L$, it is revealed that the coefficient of variation of the diffusion coefficient decreases, approaches a minimum, and then begins to increase again. This phenomenon is graphically illustrated in Figure 1 for the values given in Table I and for other values not listed.

The value of $1/L$ that results in the minimum coefficient of variation of the diffusion coefficient can be determined either graphically from Figure 1 or by the use of numerical methods. The latter technique reveals that the value of $1/L$ that results in a minimum value of %CV is 0.02585, or $L = 38.7$. The mean diffusion coefficient determined at this value of $1/L$ is 4.11×10^{-11} cm²/s with a %CV of 6.44. The parameter estimate¹¹ for the diffusion coefficient of Disperse Red 11 obtained under infinite bath conditions by the use of eq. (18) when $E_\infty = 0$ and $L = \text{infinity}$ is 3.90×10^{-11} cm²/s. The two values closely agree and are significantly higher than the mean value of 2.75×10^{-11} cm²/s given for the data of column three in Table I. The improper application of the conventional finite bath diffusion equation solutions to systems having a boundary

Table I Diffusion Coefficient, $D \times 10^{-11}$ cm²/s, as a Function of M_t/M_∞ and Time for Various Values of $1/L$ (Radius of Fiber = 1.063×10^{-3} cm)

Time (min)	M_t/M_∞	D Values for $1/L$ of						
		0.00	0.01	0.02	0.025	0.03	0.04	0.05
0.5	0.200	1.03	2.10	3.09	3.57	4.04	4.96	5.85
1	0.331	1.79	2.84	3.84	4.32	4.80	5.73	6.64
2	0.442	2.02	2.84	3.63	4.02	4.40	5.14	5.87
4	0.595	2.74	3.45	4.14	4.48	4.82	5.48	6.13
6	0.650	2.60	3.18	3.74	4.01	4.29	4.83	5.36
8	0.717	3.04	3.59	4.13	4.40	4.66	5.18	5.70
10	0.735	2.76	3.22	3.68	3.91	4.14	4.59	5.03
15	0.815	3.32	3.75	4.17	4.38	4.59	5.01	5.42
20	0.834	2.91	3.25	3.60	3.77	3.94	4.28	4.62
30	0.892	3.29	3.59	3.90	4.05	4.19	4.50	4.80
40	0.921	3.37	3.63	3.90	4.04	4.17	4.44	4.71
50	0.940	3.41	3.66	3.85	3.95	4.06	4.31	4.62
60	0.954	3.45	3.67	3.89	4.00	4.11	4.35	4.59
Mean		2.75	3.29	3.81	4.07	4.32	4.83	5.33
%CV		26.74	14.26	7.50	6.44	6.93	9.69	12.55

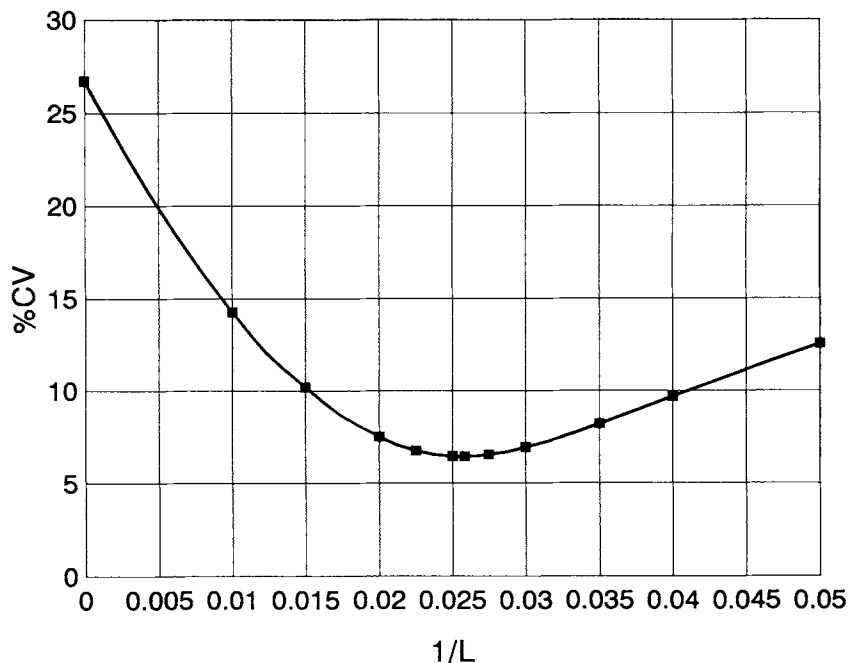


Figure 1 Coefficient of variation (%CV) of the diffusion coefficient as a function of $1/L$.

layer influence will result in an underestimation of the diffusion coefficient. The underestimation can be much more severe than that revealed in this study.

As shown in Figure 2, the trend line produced when the diffusion coefficient is plotted vs. the frac-

tional dye uptake has a slope of zero at the optimum value of L , indicating the statistical constancy of the diffusion coefficient. However, a positive slope is observed when $L = \text{infinity}$ and a negative slope is revealed when L is much lower than the optimum value.

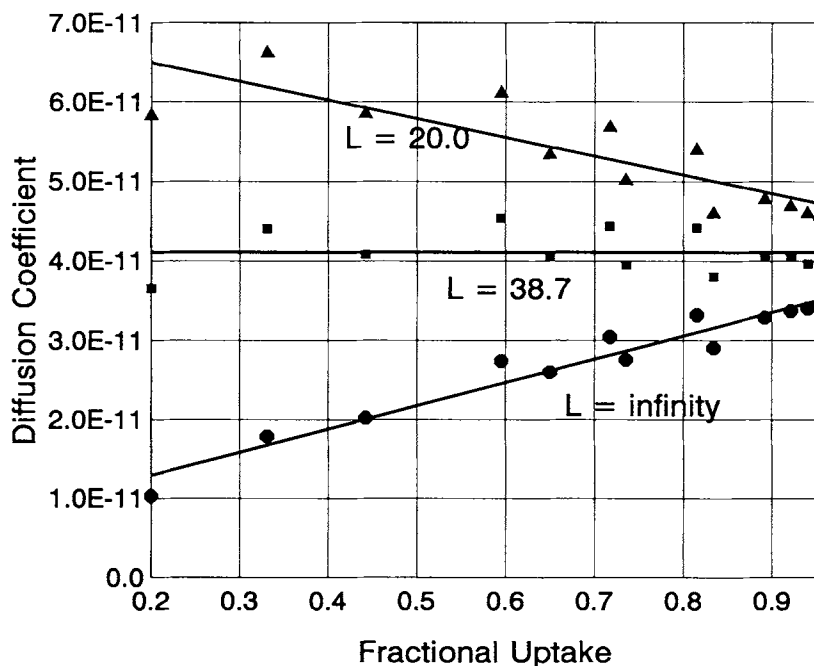


Figure 2 Trend lines produced when the calculated diffusion coefficient is plotted as a function of M_t/M_∞ for optimum and nonoptimum values of L .

CONCLUDING REMARKS

The assumption that no diffusional boundary layer exists for diffusant sorption from finite baths may not hold for real experimental systems—even when the rate of flow of the external bath appears to be sufficiently high to eliminate boundary layer influences. Sorption or desorption of diffusants by polymeric cylinders under finite bath, boundary layer conditions can be described by the use of eq. (21). The statistical technique presented can be coupled with the results of the computations made with eq. (21) to estimate the diffusion coefficient and the dimensionless boundary layer parameter simultaneously.

REFERENCES

1. A. H. Wilson, *Philos. Mag.*, **39**, 48 (1948).
2. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975, pp. 44–103.
3. P. C. Carman and R. A. W. Haul, *Proceed. R. Soc.*, **222A**, 109 (1954).
4. A. Urbanik, *Text. Chem. Color.*, **21**(6), 33 (1989).
5. A. B. Newman, *Trans. Am. Instit. Chem. Eng.*, **27**, 203 (1931).
6. R. McGregor, *Diffusion and Sorption in Fibers and Films*, Academic Press, New York, 1974, Vol. 1, pp. 172–192.
7. A. V. Hill, *Proceed. R. Soc. Ser. B*, **104**, 39 (1928).
8. J. N. Eppers, *J. Appl. Polym. Sci.*, **42**, 1519 (1991).
9. J. N. Eppers, *Indust. Eng. Chem. Res.*, **30**, 589 (1991).
10. J. N. Eppers, *J. Soc. Dyers Colourists*, **107**, 114 (1991).
11. R. McGregor and J. N. Eppers, *Text. Chem. Colorist*, **11**(9), 202 (1979).
12. M. Hou, A. K. Sarkar, and L. Fang, in *Book of Papers (Proceedings)*, 1991 AATCC International Conference & Exhibition, American Association of Textile Colorists and Chemists, Research Triangle Park, NC, 1991, pp. 42–48.
13. J. N. Eppers, *J. Soc. Dyers Colourists*, **97**, 170 (1981).
14. M. White, PhD Thesis, Clemson University, 1975.

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